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Solvent Vapor Emission Control

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For business operations that include the wet coating of a surface, followed by drying, the amount of volatile organic compound (VOC) released to the atmosphere is important. Increased awareness of ambient air quality, and various regulations affecting solvent vapor emissions do not change the need to make a business economically profitable.

36.1 Regulatory Background

For a perspective on the VOC regulations, the government now monitors ambient air quality to measure several contaminants: particulates (dust), sulfur dioxide (SO_2), ozone, and others. The amount of ozone is associated with "smog" and volatile organics in the air; it is most noticeable on hot summer days and in metropolitan areas. Industrial coating operations are important point sources that may emit tons of VOC. Automotive traffic and refueling release much more VOC, but the thousands of smaller sources are not as easy to control.

The federal Clean Air Act of 1961 promulgated an important set of regulations that establish limits and also require the states to act to meet ambient air quality standards. State regulations may be more stringent than federal regulations, but not less. Also, local regulations, such as county, municipal, or regional authority, may be more stringent. In some areas, the state or local authorities are judged by some to be too lenient toward emissions and by others to be antibusiness in enforcement of regulations. In many areas, the industrial emissions have been reasonably well controlled, but the ambient ozone standard of 0.12 ppm ozone has not been attained. (This is unrelated to the "ozone depletion" problem at high altitudes.)

The federal government now discriminates between "attainment areas" and "nonattainment areas." Regulations also discriminate between New Sources and Existing Sources. New source performance standards may be based on a cost–benefit analysis, but in some nonattainment areas, a more stringent LAER (lowest achievable emission rate) may be required, to be negotiated on a case-by-case basis. Existing sources and some new sources may be subject to RACT (reasonable available control technology).

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Typically, a state agency will control the permit applications and approval for an industrial operation. However, it must be determined locally what regulations and limits are applicable and who will control the permitting process.

36.2 Alternative Control Processes for Volatile Organic Compounds

The business and process decisions facing those who apply and dry a wet surface coating to a product require consideration of several factors, including the following:

1. Product quality needs
2. Safety
3. Regulatory and air quality restrictions
4. Costs
5. Ease and reliability of operation

The process alternatives include the following:

1. Reformulation
   A. Conversion from solvent-based to a water-based wet formulation
   B. Conversion to a high solids formulation with little or no volatile component
2. Vapor destruction
   A. Thermal oxidation of the organic compound to produce carbon dioxide and water vapor
   B. Catalytic oxidation
3. Vapor recovery
   A. Absorption–desorption using activated carbon
   B. Direct vapor condensation

Reformulation has been the subject of considerable research, which is beyond the scope of this chapter. Much success has been achieved, but in many cases, the use of VOCs gives a superior end product quality or advantage. Safety in handling solvents and costs require examination.

Vapor destruction, or oxidation, typically requires less capital expense than vapor recovery, but the extra cost for recovery facilities may be cost justified if an appreciable amount of solvent can be reused, reducing the required annual purchase of new solvent. If oxidized, some heat energy may be recovered from the solvent, but in all cases, additional energy must be purchased to operate the vapor oxidizer.

Where carbon adsorption–desorption facilities are used to recover solvents, it sometimes costs more to recover the solvent than to purchase new solvent; such extra costs are justified by the need to avoid air pollution.

There is no control process that is preferred for all situations. It is necessary to consider specific cases to determine what will be preferred. Typically, however, thermal oxidation will be preferred for smaller rates of vapor emissions or where the solvent cannot be reused, and catalytic oxidation will be considered only where the airflow required for fume capture leads to relatively dilute vapor concentrations. Solvent recovery by direct vapor condensation will be preferred where larger amounts of vapor can be reused and new dryers are planned.

36.2.1 Safety

Process safety while handling volatile organic compounds requires sure methods of avoiding fire and explosion damage.

The conventional procedure, in which solvent-based coatings are applied and dried, is to sweep the organic vapors away with an excess airflow, such that the vapor concentration is too low to sustain combustion, should an ignition temperature develop.

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Typically, at least 300 to 400 volumes of air are used to dilute one volume of vapor so that it cannot be ignited, and it is not uncommon to use several thousand volumes of air per volume of vapor.

It should be understood, however, that fire and explosive hazards also can be controlled by maintaining an oxygen concentration too low to sustain combustion. The common solvents will not ignite or sustain combustion in an atmosphere containing less than 10 to 13% oxygen (versus air with 21% O_2). This control procedure is a key to an economical condensation solvent recovery process.

36.2.2 Operating Costs

The cost for controlling vapor emissions is largely dependent on the amount of air that is admixed with the vapor. Excess air can provide the advantage of more assured safety and/or greater percentage of vapor capture in a fume hood, but the excess air greatly adds to the cost of removing the vapor from the air.

In industrial operations that incorporate a vapor incinerator or vapor recovery system, it is important to minimize the flow of dilution air to a degree that does not sacrifice safety. For example, toluene vapor in concentrations below 1.2% vapor in air are too lean to sustain combustion if ignited, and toluene vapor concentrations above 7.1% are too rich to sustain combustion if ignited. These limits are called LEL (lower explosion limit) or LFL (lower flammable limit), or UEL or UFL for the upper limits. Other solvents have slightly different limits, which are applicable under "normal" dryer conditions up to 200°F.

It is common practice to ensure that a dryer exhaust flow is not more than 25% LEL (a fourfold safety factor) to minimize the risk of combustible mixtures within the dryer. The National Fire Protection Association standards will permit vapor concentrations "not to exceed 50% of the LEL," provided a continuous indicator and alarm setup is arranged to shut the system down at a somewhat lower wet point. However, when the average exhaust concentration is in the range of 40 to 50% LEL, the absence of higher concentrations within the dryer cannot be guaranteed. Relatively few dryers are normally operated with 40% or higher LEL vapor concentrations.

On the other hand, where printing is applied to a small percentage of a surface, such as in a multicolor rotogravure line or flexographic line, it is typical for substantially more air to be used per unit of solvent applied, and for the total exhaust mixture to be relatively low in LEL concentration.

Effective vapor capture sometimes requires more airflow than the LEL safety consideration.

36.3 Vapor Oxidation

Most of the common solvent vapors may be oxidized and converted into clean and harmless carbon dioxide and water vapor. However, chlorinated solvents would produce objectionable hydrochloric acid vapors if oxidized.

A thermal oxidizer typically is operated in the 1200 to 1500°F range, with a hot gas retention of 0.3 to 0.6 sec to achieve substantially complete oxidation of the organic materials.

Catalytic oxidizers typically are operated several hundred degrees cooler than thermal oxidizers, with temperatures depending on the specific catalyst used and the concentration of vapors oxidized.

The more expensive noble metal catalysts, such as platinum, will tolerate temporarily higher temperatures than cheaper catalysts, which are susceptible to thermal deactivation. Some impurities in the air may poison any catalyst.

The heat energy released by the vapor oxidation may, in some cases, be useful for heating the process dryers or ovens. Usually, the high temperature gases from the oxidizer are used to preheat the cooler vapor-laden air, and residual heat is still sufficient to process needs.

The cost of oxidizing a given amount of vapor depends on how much dilution air is present or, for a given amount of air, how much vapor is present. More air requires a larger incinerator to retain the hot gases for the minimum time required to complete the oxidation reaction, and more energy is required to bring the air to the combustion (oxidation) temperature.

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TABLE 36.1 Operating Variables[a] for Thermal and Catalytic Incinerators

Variable	Type of Incinerator				
	Thermal			Catalytic	
LEL in exhaust, %	40	25	10	10	5
Volume of exhaust, ft^3/min	208	333	833	833	1667
Assumed exhaust temperature	200	200	200	100	100
Assumed combustion temperature	1400	1400	1400	900	900
Temperature rise required	1200	1200	1200	800	800
Temperature rise resulting from vapor oxidation	1160	725	290	290	145
Temperature rise required from preheater or auxiliary fuel	40	745	910	510	655
Requirement from preheater or other fuel, Btu $\times 10^3$/h	9	170	820	460	1180
Available temperature differential across heat exchanger (with no other fuel used)	1160	725	290	290	145
Ratio of heat exchanger area[b] required (to avoid auxiliary fuel consumption)		1	12	6.75	35

[a] All temperatures in degrees Fahrenheit.

[b] Assuming equal coefficient; $A = Q/\Delta T$, where A = the heat transfer area, Q = heat flow, and ΔT = temperature differential.

However, if the vapor concentration is maintained close to 40% LEL or above, the solvent vapor can supply substantially all the energy required. At lower concentrations, it becomes increasingly necessary to supply auxiliary fuel or to provide more air–air heat transfer to preheat the vapor laden air.

For example, one cubic foot of toluene vapor diluted with more or less air in the exhaust flow to be incinerated will be as shown in Table 36.1.

From Table 36.1, it can be appreciated that a reduction in airflow (for a given flow of solvent vapor) will proportionately reduce the size of the vapor incinerator, but the size of heat exchanger or the amount of added fuel required is affected to a much greater degree.

It is theoretically possible to provide enough heat exchanger capacity to obviate the need for additional fuel for normal operation. In practice, an auxiliary fuel burner is needed for start-up, and it must be kept ignited and ready to heat the air when the vapor concentration decreases.

Heat exchangers for vapor thermal oxidizers usually are the shell-and-tube type, using stainless steel tubes, or ceramic beds. Some metal plate–plate exchangers also are used, but in every case, it is important to prevent leakage or short-circuiting of vapor-laden air to the exhaust gases, or bypassing the combustion zone. Such leakage or bypassing can generate objectionable odors from partially oxidized organics.

The ceramic bed heat exchangers operate by periodically reversing the flow direction through at least two or more beds, which are alternately heated and cooled. Outgoing hot combustion gases flow through a bed until the ceramic pieces reach a set temperature, then the flow is reversed and vapor-laden gases are heated so they flow through the hot bed into the combustion zone. There is no problem if the vapor-laden gases ignite in the bed prior to the combustion space, but before flows are switched back, it is desirable to first purge vapor-laden gases from the cooking bed into the combustion zone. Nonoxidized vapors should not be pushed out with exhaust flow. With relatively large beds, it is practical (but not inexpensive) to provide the high heat transfer area needed to accommodate relatively dilute vapor flows. The bed size required can be minimized by a high frequency of flow switching; the airtight dampers may be switched every few minutes. The ceramic pieces must be selected to tolerate frequent temperature changes and to accommodate the thermal expansion–contraction cycle that occurs. If dust is released by thermal movements or abrasion, it may prevent direct usage of the residual hot gases in the dryers and ovens.

Metal surface heat exchangers, with hot combustion gases in one side and the cooler vapor-laden gases on the other side, operate continuously, without flow reversal or switching dampers. Thermal expansion–contraction can be a problem, leading to torn welds or fractures and to leakage of the higher pressure vapor-laden air into the lower pressure oxidized discharge flow. Such leakage can generate objectionable odors by the scorching of the vapors.

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In heat exchangers of the shell-and-tube type, longer tubes with baffled counterflow over the tubes are more efficient than short tubes with cross-flow.

A recent development, patented by the Wolverine Corporation (Merrimac, MA), overcomes the expansion problem with long-tube heat exchangers; the tube is free to expand and contract at one end within a slip tube that acts as an air aspirator. In this arrangement, a small amount of lower pressure oxidized vapor is allowed to leak back into the oxidation zone; leakage in this direction is acceptable.

36.4 Solvent Recovery

Solvent recovery may be preferred to vapor oxidation if the solvent can be reused, allowing a company to save substantially on the purchase of new solvent. Although vapor oxidation can return some energy value from the solvent, usually the "chemical" value is appreciably more than the energy value.

There are two important approaches to solvent recovery: activated carbon and direct condensation. The carbon approach is substantially more costly. The condensation approach is not always applicable, but it can be much less expensive when the dryers for a coated web and condensers are designed as a system.

36.4.1 Carbon Adsorption

When a carbon bed is installed to capture solvent vapors exhausted with air from a dryer, it is usual to provide two or more carbon beds and to periodically desorb from one while adsorbing in the other(s). Desorption is accomplished by heating the bed and sweeping the vapors out, typically with steam.

The steam and vapors are then condensed, and the steam condensate (water) must be separated from solvent. Typically about 3 to 4 or up to 10 lb of steam is used per pound of solvent recovered. If the recovered solvent is soluble in water (alcohols, ketones, etc.), the need to separate the water presents additional expenses. Some vapors, such as methyl ethyl ketone, absorb onto carbon with so much heat release that precautions are needed to prevent spontaneous ignition from burning up the air-swept carbon bed.

There are many carbon adsorption systems in which the value of solvent recovered exceeds the cost of operation. Often, however, it costs more to recover the solvent than to buy new solvent. In such cases, the higher recovery cost is charged to the need to avoid air pollution.

36.4.2 Direct Vapor Condensation

Direct vapor condensation can be more economical than using carbon beds for solvent recovery. The energy consumption is usually less than 10% of the energy to operate a conventional air-swept dryer and carbon bed, and there is no water added to the solvent by the process. Also, there is no exhaust flow to the atmosphere in the preferred designs. The vapor condensers are much smaller than required for carbon bed recovery system, and there is another advantage in that when two or more dryers are operated with different solvents or blends of solvents, separate vapor condensers avoid the mixing of solvents and the costs of separating them. Usually, a water chiller type of refrigeration system is required, but one system can serve all the condensers.

However, there are limitations on the applicability of this process: the process dryers must be substantially "airtight" to permit the contained atmosphere be recirculated countless times with a minimum of interchange with outside atmosphere. Indirect heaters, such as steam coils, are necessary. Also, the oxygen level in the contained atmosphere should be kept below the limit (10 to 13% O_2) that would sustain combustion; otherwise, it is necessary to use very cold condensers and relatively high recirculation rates to keep the vapor levels safely below the vapor LEL limits. There is a need for a relatively small flow of inert (low oxygen content) gas to offset the tendency for the wet web to drag air (21% O_2) into the dryer, and it is necessary to maintain a ready reservoir of pressurized inert gas (a) to facilitate a rapid air purge and dryer start-up after the dryer has been opened for any reason, and (b) to provide a safety cushion for a fail-safe shutdown during an electrical power outage.

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The sources of inert (low oxygen) gas required include the flue gas of a gas-fired steam boiler and purchased liquid nitrogen or carbon dioxide. Where flue gases are used, the gas burner must be of the type that can maintain a low ratio of excess air to fuel for various fuel firing rates. A compressor and pressurized storage tank can provide the ready reservoir for last start-up and fail-safe shutdowns, or a tank of liquid nitrogen with vaporization facilities can be used.

In some important respects, the operation of an inerted airtight dryer is inherently safer than a conventional air-swept dryer. In an air-swept dryer there is a transition zone between a flammable wet interface and a nonflammable exhaust, and there is the potential for a temporary excess solvent loading into the dryer to produce a large volume of combustible mixture. In an inerted dryer, there is no flammable interface, and any temporary excess solvent loading will not make a combustible mixture. When the coating process and wet web is stopped for any reason, there is no tendency for outside air to exchange with the atmosphere contained in the dryer, except as air may be drawn in to replace the volume of vapor condensed, or to make up for gas volume contraction as the contained gas cools down. In the Wolverine systems, the normal operating vapor concentration in the dryer is designed to prevent the condensation due to vapor volume of any unsafe air inhalation into the dryer. Normally, the vapor condenser temperature is selected to draw the vapor concentration below the organic LEL level when the coating process is stopped. This then provides a double safety factor with both a safe O_2 LEL level and a safe organic-in-air LEL level.

When a dryer is shut down overnight or for a weekend, it is not necessary or desirable to purge the contained atmosphere to the outside atmosphere.

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